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ANNUAL AND SEMI-ANNUAL STATUS REPORT

on

SPECTROSCOPY AND REACTIONS OF  
MOLECULES IMPORTANT IN CHEMICAL EVOLUTION

to

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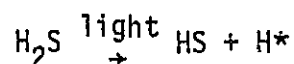
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## I. INTRODUCTION

The primary broad goals of the research are to investigate (1) hot hydrogen atom reactions in terms of the nature of products produced, mechanism of the reactions and the implication and application of such reactions for molecules existing in interstellar clouds, in planetary atmospheres, and in chemical evolution; (2) photochemical reactions that can lead to molecules important in chemical evolution, interstellar clouds and as constituents in planetary atmospheres; (3) spectroscopic and theoretical properties of biomolecules and their precursors and where possible, use these to understand their photochemical behavior.

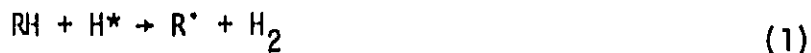
Hot hydrogen (H) atoms are those which have translational energy (kinetic energy) in excess of that expected if they were in thermal equilibrium with their surroundings. The hot H atoms could be from any source, including photolysis of molecules such as HBr, HCl, H<sub>2</sub>S and CH<sub>3</sub>SH:



where H\* is a hot H atom. Commonly from the point of view of chemical interest, the energy range for hot H atoms extends from ~0.3 eV (7 kcal/mole) to 10 eV (230 kcal/mole).

The observed primary reactions of hot H atoms denoted as H\* are as follows<sup>1,2,3</sup>:

abstraction of hydrogen atoms



where  $R^*$  is an alkyl free radical

substitution reactions



where D is deuterium atom.

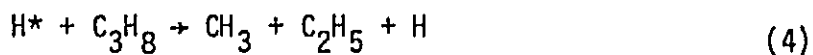
addition reactions



where  $C_2H_5$  is ethyl radical and is

commonly formed vibrationally hot,

fragmentation reactions



Threshold energy is essentially the lowest energy at which a certain reaction begins to have a finite probability of occurrence. Threshold energies though related to activation energies cannot be calculated without insight into the mechanism of energy transfer resulting in the breaking of a bond and formation of another. Nonetheless, if a complex exists at an energy near the threshold energy, the threshold is at least equal to the activation energy multiplied by  $\frac{m + M}{M}$  where  $m$  is the mass of H and  $M$  is the mass of the reacting molecule (assuming no translational to rotational or vibrational energy transfer occurs)<sup>1</sup>. Generally, the threshold energy for H atom

abstraction from saturated aliphatic hydrocarbons is 0.25-0.35 ev (6-8 kcal/mole). The activation energy for H atom abstraction from  $\text{CH}_4$  is 12 kcal/mole and is 8 kcal/mole for  $\text{C}_2\text{H}_6$ .<sup>4</sup> Some other activation energies for H abstraction from molecules of interest in this study are<sup>4</sup>:

$\text{H}_2\text{O}$ (g)	20 kcal/mole
$\text{NH}_3$ (g)	18 kcal/mole
$\text{H}_2\text{S}$ (g)	2-3 kcal/mole
$\text{CH}_3\text{SH}$ (g)	203 kcal/mole

The efficiency of abstraction of H from a hydrocarbon to make  $\text{H}_2$  using hot H atoms is some  $10^5$  times greater than that using thermalized H atoms at room temperature<sup>5</sup>. The average probability of reaction of a hot H atom with propane for example is 18% and approximately 50% of the time, the reaction is H atom abstraction (for hot H atoms in the 2-10 ev range)<sup>6</sup>. These percentages vary somewhat depending upon the hydrocarbon.

Some 27 molecules (including radicals and ions) have been discovered in interstellar space and of these, approximately 20 are organic molecules of varying complexity. In addition, there are indications that  $\text{CH}_4$  has been detected by absorption in the infrared<sup>7</sup>. Furthermore, it has been very recently stated<sup>9</sup> that "at this time there is no quantitative theory for formation of polyatomic

molecules" and "...interstellar chemistry... requiring new insights into the basic understanding of chemical reactions."

Radio observations indicate that interstellar molecules are associated with clouds which contain gas and dust (primarily silicates). The temperature of dust grains is estimated to be 80°K. The temperature of the HI (neutral hydrogen) clouds is believed to be in the range of 50-125°K. In general, temperatures can be as low as 6°K and as high as 45°K in large molecular clouds. The molecular clouds have a density of  $H_2$  of the order of  $10^3$ - $10^4$   $cm^{-3}$ , a size of 10-100 light years and masses in the range  $10^4$ - $10^5$  solar masses (1 solar mass is  $2 \times 10^{33}$  g).<sup>8</sup> The density of most of the organic molecules observed in molecular clouds are some  $10^7$  less than for  $H_2$ , except for CO, which is equal to  $H_2$ .

At least two major considerations<sup>9,8</sup> point to the fact that polyatomic molecules were formed or released in the clouds where they presently occur. The lifetimes of molecules in clouds with a few magnitudes of extinction become of the order of  $10^6$  years.<sup>8</sup> Interstellar clouds are estimated to have lifetimes of approximately  $10^7$  years which is about 2 to 3 orders of magnitude less than that of the galaxy.

The time scale for three body gas phase reactions under the conditions of the low density in interstellar space ( $<10^6$   $cm^{-3}$ ) is greater than  $10^9$  years. In light of this fact, chemical reactions

are limited to occurring by two-body gas phase collisions or take place on the surface of the dust particles. Furthermore, the conditions in interstellar space for formation of molecules are substantially displaced from thermodynamic equilibrium.<sup>9</sup>

Because the area of photochemistry is much more broadly known, no detailed discussion of its aspects will be given. Its application in chemical evolution are well founded as for example, in the review of reference 10. Recent examples of the use of photochemistry includes that of Ferris and Kuder<sup>11</sup> and Becker et al<sup>12</sup> involving the formation of imidazoles (also see later discussion, section II and III). It is nonetheless worthwhile to point out that there has been almost no concern with control of wavelength for photochemistry except in a few instances, for example, see reference 12. Furthermore, relatively little attention has been given to the spectroscopic properties of the substrate molecules or mechanisms of the reactions.

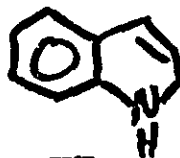
Many techniques including conventional electrical discharge, ultraviolet irradiation, and heating of various simple molecules have resulted in production of some biologically significant molecules<sup>10,13,14,15</sup>. More recently, ultraviolet irradiation of a mixture of  $H_2S$ ,  $NH_3$ ,  $CH_4$ , and  $H_2O$  gave polymeric sulfur and if  $C_2H_6$  was added, principally organic sulfur compounds resulted.<sup>16</sup> Similar experiments<sup>17</sup> have been reported to give some amino acids

provided  $C_2H_6$  was present, with the implication that superthermal H atoms appeared to initiate reactions leading to the amino acids.



## II. SUMMARY OF PRECEDING RESEARCH

The spectroscopy, photochemistry, and theoretical calculations of variously substituted and benzo condensed chromene (I) as well as the spectroscopy of photochemistry of variously substituted dihydroquinoline (II) have been completed.

**I****II**

Essentially all compounds give a colored intermediate at low temperatures ( $-100^{\circ}\text{C}$  to  $-196^{\circ}\text{C}$ ) which thermal reverts to the original compound. The nature of the intermediate in each of the two classes has been identified. Several compounds exhibit this same behavior at room temperature as well. Several of the chromenes exist as natural plant products and because of the reversible nature of their photochemistry, may play a role in controlling plant processes.

Because formaldehyde has been strongly implicated as a substrate in reactions of interest in chemical evolution and does occur in interstellar clouds and planetary atmospheres, a spectroscopic study of it was completed. This research included various solvents including water and solid substrates. Furthermore, although there are multiple examples in the literature of reactions

of formaldehyde in solution, none appeared to exist for the gas or the common polymer of formaldehyde, paraformaldehyde.

Absorption, emission, and NMR studies indicate that: (1) formaldehyde exists as a monomer (form A) in nonpolar solvents to a temperature of approximately  $-95^{\circ}\text{C}$ , (2) at  $-95^{\circ}\text{C}$  in nonpolar solvents, formation of a formaldehyde polymer (form C) begins which is thermally reversible at temperatures  $>-90^{\circ}\text{C}$ . The form C also exists at room temperature in water, dimethyl sulfoxide, dimethylformamide, and tetrahydrofuran. (3) Formaldehyde can act as a hydrogen-bonding donor or acceptor in a complex with solvent molecules or silica gel (form B). In aromatic hydrocarbons, formaldehyde acts as a donor whereas in 2-methyltetrahydrofuran, chloroform, and silica gel it acts as an acceptor. Also, in 2-methyltetrahydrofuran, forms A and B exist in addition to C. Monomer formaldehyde exhibits a fluorescence from the lowest  $S_{n,\pi^*}$  state in nonpolar solvents to  $-95^{\circ}\text{C}$ . Both the forms B and C exhibit emission. In addition to the classification of the forms of formaldehyde, it is possible to classify the solvents into four main groups based on the rate of formation of paraformaldehyde or the fact that formaldehyde essentially totally reacts (strong hydrogen-bond donors or molecules with active  $\alpha$ -hydrogen atoms such as water and alcohols).

Both paraformaldehyde (solid) and formaldehyde (gas) undergo

reactions in the presence of several inorganic compounds to generate a variety of interesting organic products that can be important in chemical evolutionary processes. Inorganic compounds with which reactions occur are zinc oxide, zinc chloride, magnesium oxide and magnesium chloride. Silicon dioxide, ferric and ferrous oxides do not react to give detectable products. These inorganic compounds were chosen because all of the metals occur in the earth's crust, in meteorites and some in the moon's crust. Fifteen organic compounds have been detected as reaction products including acrolein, acetaldehyde, methyl formal, formic acid, glycolaldehyde and methanol.

Organic compounds are produced at temperatures as low as 56°C (lowest attempted) and in high yield, up to 75% (based on the weight of paraformaldehyde used). The quantity produced depends principally on (1) the nature of the inorganic compound, (2) the ratio of the inorganic compound to paraformaldehyde, (3) temperature and (4) reaction time. The percent distribution depends on the factors (1) and (3). It also appears that the time of analysis after completion of a reaction affects the results. Although yields are lower from formaldehyde than paraformaldehyde, we believe this is a matter of poor diffusion of the gas through a solid bed.

Acrolein is the first member of an unsaturated aldehyde series



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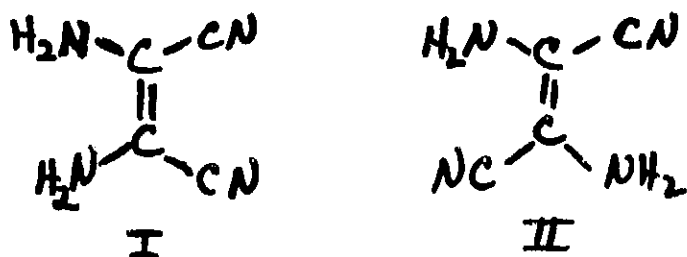
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The quantum yields of fluorescence ( $\phi_F \sim 0.007$ ) and phosphorescence ( $\phi_P \sim 0.00004$ ) indicate that excitation results in nearly complete internal conversion and/or photochemistry. Theoretical calculations have been made including the potential energy curves resulting from twisting around the central carbon-carbon single bond as well as the terminal carbon-carbon double bond. It appears that photoisomerization cannot occur around the single bond in either the  $\pi, \pi^*$  or  $n, \pi^*$  states but could occur around the double bond in the lowest  $\pi, \pi^*$  triplet state. In the latter case, a potential energy minimum exists near  $90^\circ$  and degeneracy occurs with the ground state.

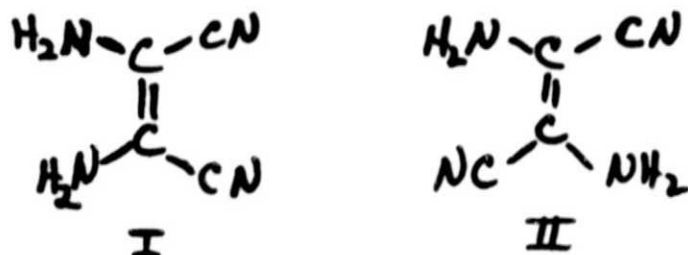
Diaminomaleonitrile (III) and diaminofumaronitrile (IV) are respectively substituted cis and trans ethylenes



Photocyclization of diaminomaleonitrile can occur to give a substituted imidazole and has been thought to be a step in the chemical evolution of purines.<sup>11</sup> Based on a wavelength study of the excitation of pure diamino-fumaronitrile (DAF) in a polar solvent, we conclude that either (1) DAF cannot form 4-amino-5-cyanoimidazole (ACI) but can be converted to diaminomaleonitrile

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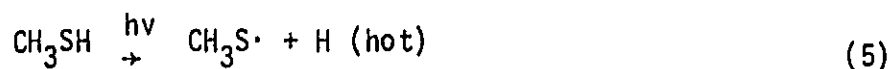
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(DAM) which can or (2) there is a wavelength dependence for the formation of ACI from DAF. The highly dominant result of irradiation of DAF at wavelengths well within the absorption onset is trans (DAF)  $\rightarrow$  cis isomerization to produce DAM. Irradiation of initially pure DAM in a polar solvent at wavelengths within (but relatively near) the absorption onset results in photoisomerization to DAF and production of the imidazole, ACI. The photochemical formation of ACI has an overall activation energy which is larger than that necessary for isomerization. There is evidence for the existence of an intermediate(s) between DAM (also potentially DAF) and ACI. Excitation of DAM or DAF in a rigid matrix at  $-196^\circ$  produces a species which has been assigned as aminocyanocarbene, in addition to photoisomerization (but no ACI).

Certain results on the hot H atom chemistry were completed prior to the current year research program. Hot H atoms in our case were produced by the photolysis of a donor molecule as



The hot H atoms had kinetic energies in the range of 17-32 kcal/mole. In our case, the primary hot H atom reaction of interest was



The hot H atoms initiated reaction in mixtures of simple gases

chosen from among  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$ . In two cases,  $\text{C}_2\text{H}_5\text{OH}$  was chosen as a substrate because of its production in hot H atom reaction. The results will only be briefly summarized since more detail will be given in section III which will include results of current programs as well.

Hot H atoms initiated reactions to produce organic alcohols, amines, and acids, amino acids and other compounds (principally organic sulfur ones). Photolysis of either  $\text{H}_2\text{S}$  or  $\text{CH}_3\text{SH}$  was used as hot H atom sources. Typical quantum yields of formation of protein amino acids were  $2\text{-}4 \times 10^{-5}$ . Amino acids were detected and identified up to this time utilizing a commercial amino acid analyzer (Technicon). The one carbon atom substrate  $\text{CH}_4$  was found to be sufficient to produce amino acids and a two carbon substrate was not a necessity as has been previously stated.<sup>17</sup> We have proposed that free radicals were initially produced by the attack of the hot H atom on the substrates as in reaction (6). In turn, the free radicals attacked other reactants ultimately leading to various products. It was also proposed that hot H atoms could be initiators of reactions in interstellar (space) for formation of molecules are known to be substantially displaced from thermodynamic equilibrium.<sup>9</sup> Consequently, despite any low ambient temperatures, and because



of the low density of atoms (and molecules and dust), a hot atom could exist and remain hot for a very long time. Collision of this hot atom with a molecule could result in reaction followed by further subsequent ones. More on these points will be given in section III.

### III. RESULTS OF CURRENT YEAR RESEARCH

#### A. Hot H Atom Reactions

We have concentrated on three areas in this research this year (1) nature of products resulting from hot H atom initiated reactions, (2) importance of the products from these reactions in chemical evolution, in planetary atmospheres and in interstellar space (clouds), and (3) mechanism of formation of molecules found in interstellar space (clouds). The latter point is particularly important in view of the fact that it has been recently stated that there is no quantitative theory for formation of polyatomic molecules in interstellar space (and clouds).<sup>9</sup>

The low temperature (and density) often associated with areas of interstellar space where relatively complex organic molecules are found would seemingly preclude any type of chemistry leading to such molecules. However, we propose that hot H atoms could act as reaction initiators, although not limited solely to these kinds of hot atoms. The hot atoms could come from any source including photolysis of organic molecules already present. More will be said concerning this later. Based on this idea, we have explored a quite broad spectrum of hot H atom reactions utilizing simple molecules known to exist in interstellar

space (as  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{H}_2\text{S}$ ) as substrates; furthermore, we have identified the products and their relationship to molecules found in interstellar space. Recall that any system involving hot H atoms is in non-thermodynamic equilibrium as is the condition for formation of molecules in interstellar space. The products were also evaluated for their existence or potential existence in planetary atmospheres as well as their significance in chemical evolutionary processes.

First we shall give the results for reactions thus far studied, some of which has been recently published,<sup>18</sup> some more of which is in press<sup>19</sup> and some as yet unreported results. Table I summarizes the nature of the experiments, conditions and results using hot H atoms having an energy range of 17-32 kcal/mole. We shall comment on each of the experiments.

Experiment I was the first of our experiments to show that it was possible to obtain amino acids, including one containing sulfur using hot H atoms as initiators. In addition, other products were obtained, including amino compounds some of which were more acidic and others more basic than the protein amino acids.

Experiment II was performed under identical conditions to Experiment I without irradiation to provide assurance that no product compounds were thermally produced, particularly the amino acids. No compounds other than reactants were detected.

This experiment was considered as a blank test for all other experiments as well.

Experiment III was similar to Experiment I except  $H_2S$  replaced  $CH_3SH$  as the hot H atom source. The workup of this reaction is cleaner because of the absence of sulfide compounds. Again, several amino acids were detected, including a sulfur containing one. Also, there appears to be one more acidic and some more basic amino compounds than the protein amino acids.

Experiment IV was done to provide some insight into the intermediates and/or mechanism of formation of amino acids in addition to determining if and what products could be formed from a hydrocarbon and water. Two organic acids and ethanol were formed in addition to disulfides.

Experiment V utilized ethanol and ammonia since the alcohol had been formed as a product with ethane and water. A significant number of amino acids were produced and in fact more than in Experiment III. However, the real significance of this is not clear since there was a change in the light source used to produce hot H atoms (from  $H_2S$ ). The quantum yield of formation of the amino acids was  $\sim 2-3 \times 10^{-5}$ .

Experiment VI differed from Experiment V principally in the fact that water was present in addition to ethanol (as well as  $NH_3$ ). The distribution among the amino acids in Experiment V

was approximately equal but in Experiment VI, approximately 95% of the total was glycine. In fact, a significant absolute amount of glycine was found, 0.05 mg. The quantum yield of formation of the amino acids was  $\sim 3-4 \times 10^{-5}$ . However, it should be noted that the number and nature of the amino acids detected was the same in both experiments. Although liquid ethanol was present with the liquid water, we believe the important aspect responsible for the change in distribution of the amino acids was the water present in the gas phase compared to only ethanol in Experiment V. Possibly amino compounds more acidic and some more basic than the protein amino acids were also detected.

Experiment VIIA (not given in Table I) was similar to that of VI in terms of the nature of the substrates. The  $H_2S$  concentration was somewhat higher and the reaction was run longer ( $\sim 200$  hrs). In this case the elute from the ion exchange column was analyzed by gas chromatography-mass spectrometry. The six protein amino acids glycine, leucine, alanine, valine, aspartic, and glutamic were positively identified. In addition, eight other none  $\alpha$  type amino acids were found. Table II presents mass spectral data for glycine.

Experiment VII shows that either ethane or methane with ammonia can produce the corresponding organic amine. This experiment indicates that the amines could be intermediates in the formation of amino acids.

Experiment VIII was done since organic amines had been produced in Experiment VII and as ethanol, may be intermediates in the formation of amino acids. A number of amino acids were formed, but the number was less than with ethanol as a substrate. Whether there is any significance to this difference is not clear at this time.

Experiment IX is important regarding the fact that amino acids can result from a one carbon substrate methane and of the same number and nature as from the two carbon substrate ethane. It should be emphasized that very pure methane (99.97% min) was used as the carbon source to eliminate the possibility of contaminant ethane as the carbon source. Amino compounds more acidic and some more basic than the protein amino acids could also be present.

Experiment X was performed to determine if hot H atoms could initiate product formation with carbon monoxide and water as reactants. No produce organic compounds were detected.

Experiment XI was performed to determine what products could be detected using CO as a substrate as well as  $\text{CH}_4$ . The former of these is known to exist in interstellar space and the latter is suspected to exist.<sup>7</sup> Interestingly, two molecules ( $\text{CH}_3\text{CHO}$  and  $\text{COS}$ ) were formed that exist in interstellar space as well as one ( $\text{CS}_2$ ) which is related to one found ( $\text{CS}$ ). The

molecule  $\text{SO}_2$  is particularly interesting since the most recently molecule discovered in interstellar space is  $\text{SO}$  (September 27, 1973).<sup>20</sup> Obviously, as in the case of  $\text{CS}_2$  and  $\text{CS}$  (interstellar space),  $\text{SO}_2$  and  $\text{SO}$  are highly related species.

Experiment XII was performed to provide a thermal reaction blank test to give assurance that none of the product molecules found in Experiment XI arose because of common thermal reactions. This was particularly important regarding those molecules formed in Experiment X that do exist or are related to those that exist in interstellar space, especially  $\text{SO}_2$ , which was an unexpected product. The only product molecule detected was  $\text{COS}$ , but its concentration was a factor of 20-25 lower than that from Experiment XI. Thus all the product molecules from Experiment XI arose from hot H atom initiated reactions, except that some small amount of  $\text{COS}$  apparently arises from some unknown origin.

Experiment XIII employed an unsaturated substrate  $\text{C}_2\text{H}_4$  as a carbon source along with  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . Ethylene ( $\text{C}_2\text{H}_4$ ) can add hydrogen (hot) and commonly forms vibrationally hot ethyl radical ( $\text{C}_2\text{H}_5$ ). On the other hand H atom abstraction from  $\text{C}_2\text{H}_6$  (using hot H) usually results in  $\text{C}_2\text{H}_5$  radical which is not vibrationally hot. We wished to explore any differences in type or quantity of resulting products under such potentially different conditions for the  $\text{C}_2\text{H}_5$  radical. Although products were seen, no amino

acids were detected. However, because of experimental difficulties the reaction time was shorter than usual so that further investigation of this reaction is required before any definite conclusions can be reached. Other molecules were found, including an alkyl amine, see Table I.

Experiment XI utilizing CO and CH<sub>4</sub> (and hot H atom) appears to be a uniquely interesting reaction producing four molecules either found in interstellar space (two) or related to them (two).

All analyses were accomplished using gas chromatography-mass spectrometry and in most cases but not all (see Experiment VIA in text and Table I), amino acids were detected by a commercial amino acid analyzer.

Some important conclusions can be obtained from the results of the experiments

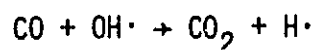
1. Hot hydrogen atoms can initiate reactions among simple molecules to produce organic molecules and biomolecules of significance.
2. The one carbon reactant methane can participate in reactions leading to the multiple carbon containing amino acids. This is an important fact because large amounts of methane existed on the primitive earth, is existent near some planets and may exist in interstellar space (clouds). The two carbon reactant is not a necessary reactant.



3. In addition to amino acids, other significantly important molecules can be produced by reactions initiated by hot hydrogen atoms such as methanol, ethanol, acetic acid, propionic acid, and methyl and ethyl amines. Furthermore, it appears that some of these could be intermediates in the production of the amino acids based on the fact that when they are used as substrates, amino acids are produced.
4. The first intermediate formed after attack by the hot H atom is a free radical. These in turn attack other reactants giving other free radicals. In some cases, the radicals combine to give products such as, for examples, ethane, ethanol, ethyl or methyl amine and dimethyl (or diethyl) disulfide. In other cases such as for the organic acids and the amino acids, the detailed mechanism is not known. In at least some cases some mechanistic ideas for the formation of products can be postulated (in addition to primary radical combinations). For example, the formation of COS is postulated to occur as



in analogy with a parallel known reaction<sup>21</sup>



In most other cases, we have not had sufficient chance to explore the significant quantity of literature on radical—molecule reactions in order to deduce or postulate mechanisms for other products. This will be one of the major goals for the next grant year.

We have proposed hot H atom as potentially important initiators of reactions leading to molecules found in interstellar space. We shall now explore further the basis for this belief.

When a system is in thermal equilibrium, we mean that the molecules are colliding very frequently and that there is an average velocity or kinetic energy for the molecules of the system and it does not change. This also means an average temperature can be defined for the system. This is the common circumstance for almost all systems where the density of molecules is high such as on earth. However, in interstellar space where the density of molecules is very low, molecules collide only rarely. If for some reason a molecule or atom attained a high velocity or kinetic energy, it could remain this way for a very long time and not be in thermal equilibrium with its surroundings (not have the same average velocity or kinetic energy as other molecules or atoms in the system). In such a case, this is a non-equilibrium system. Thus despite the fact the ambient temperature of the surroundings (all other molecules and dust) may be very low, the "temperature" of the high velocity

molecule or atom would be very high.\* The foregoing is true for any situation until the hot molecule or atom has had a sufficient number of collisions to slow it down to near the average velocity or kinetic energy (temperature) of other molecules or atoms in the system. We can produce a non-equilibrium (thermal) system in the laboratory by irradiating molecules which eject a hydrogen atom of high velocity or kinetic energy which until it has had a great many collisions, is hot and at a considerably higher "temperature" than the surroundings (other molecules). At least in this sense, we can reproduce a non-equilibrium (thermal) condition which exists in interstellar space. We are well aware of the fact that the ambient temperature and density conditions in clouds of interstellar space are low and particularly because of the former, most chemical reactions would not occur. However, recall the conditions for formation of molecules in interstellar space are substantially removed from thermodynamic equilibrium<sup>9</sup>. It is just this possibility of a non-equilibrium condition where some atom(s) are hot and not in thermal equilibrium that would permit reactions of relatively high activation energies to occur that ordinarily could not. Another fact of note is that changes

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\*The term temperature is put in quotation since the term temperature can rigorously be used for only a system in equilibrium; however, it can be roughly used to describe the velocity of kinetic energy of molecules, the higher the velocity or kinetic energy of molecules, the higher the temperature.

in temperature have only a relatively little effect on the average kinetic energy and the activation energy of reaction.<sup>22</sup> Recall there is relationship between activation energy and threshold energies (see section I); therefore, it is expected that threshold energies will be essentially temperature independent. It should be emphasized that we believe the basic idea of hot H atoms as reaction initiators is also applicable for reactions in atmospheres of planets both in the past and in the present.

We wish to comment on some specific results we obtained relative to another published study<sup>17</sup>. We have shown that amino acids can be produced utilizing a saturated hydrocarbon substrate containing only one carbon atom, namely, methane. The other study stated that the two carbon substrate ethane, was required for the formation of amino acids. It also was stated that the bulk of the amino acids from some similar experiments as described above very probably arose from hydrolysis of nitriles or polypeptides and were not made primarily in the free state. Our conditions never resulted in the formation of observable polymer nor did we employ acid or basic hydrolysis conditions anywhere in the workup-detection process. We cannot evaluate the extent of any basic hydrolysis (because of the presence of  $\text{NH}_3$ ) during the course of a reaction in which water was present. However, it is expected to be small in the water trap because of the relatively

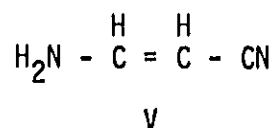
low temperature. Also, recall in one experiment, V, no water was present during the reaction and yet amino acids were found. Amino acids were made in four different experiments utilizing  $C_2H_5OH$  and  $C_2H_5NH_2$  as substrates (in addition to those with  $NH_3$ ,  $C_2H_6$ , or  $CH_4$ ,  $H_2O$ ) and considering the nature of the reactions (hot H atom), it would appear that no nitrile containing molecules could be generated. Furthermore, no HCN or nitrile containing molecule was detected in any experiment either in the gas phase or in solution (water trap). In view of these facts, we believe the major amount of the amino acids do not result from hydrolysis of a polymer but are made by a unique mechanism or mechanisms other than the presumed more conventional ones.

It would not seem unreasonable to search in interstellar space for amino acids, as well as for acetic acid, ethanol and alkyl amines. However, because of the distinctively different reaction conditions, particularly the latter molecules may not exist as such but as their precursors or subsequent reaction products. Nonetheless, the presence of formic acid and methanol give some hope that some of those mentioned could exist. The discovery of amino acids of course would be most noteworthy. Even so, the discovery of amino acids in meteorites suggests the possibility of suitable conditions for synthesis of such molecules existed and now exist in protoplanetary gas and dust clouds.

### B. Spectroscopy and Photochemical Study of Enaminonitriles

Although certain aspects of this work was completed earlier, we have extended the breadth of the molecules studied and added results verifying the nature of the photochemical products.

The molecule cis -  $\beta$  - aminoacrylonitrile (V), hereafter called cis- $\beta$ -AAN,



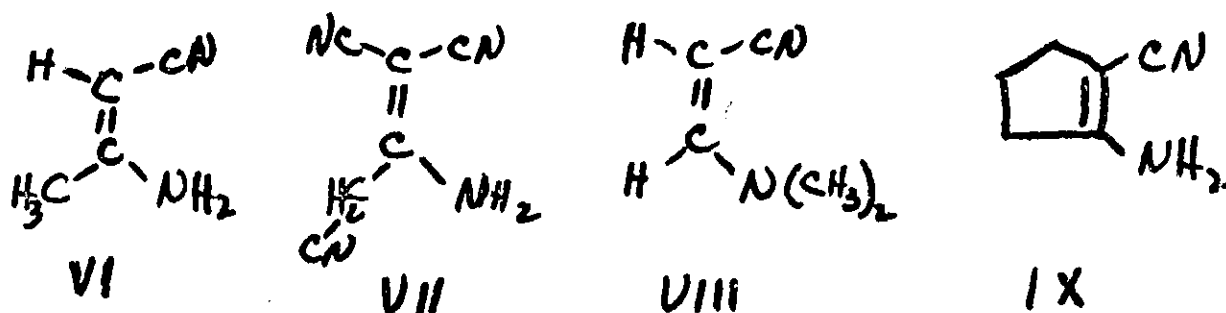
has been synthesized from cyanoacetylene and ammonia at dry ice temperatures and aqueous ammonia at 0°C. Although synthesis of this had been reported earlier,<sup>23</sup> it had not been isolated nor identified. In view of the fact that this molecule can be made from two molecules that exist in interstellar space and the fact that it potentially can undergo photolysis to form imidazole, we wished to verify its existence as a stable entity.

The ammonia-cyanoacetylene adduct was identified firstly as aminoacrylonitrile based on mass spectral analysis (parent ion peak at mass 68) infrared spectroscopy (all essential group frequencies were identified) and ultraviolet spectroscopy (one strong band located as expected). The most unequivocal assignment of the adduct as that of cis- $\beta$ -AAN was obtained from NMR spectroscopy, including the use of D<sub>2</sub>O as a solvent to

obtain deuterium exchange of the amino protons with a corresponding disappearance of the amino proton signal. At the same time, the spectral complexity of the signal associated with the proton on the carbon adjacent to the amino group simplified as expected because of the lack of coupling with the replaced protons on nitrogen.

It was possible to identify photoinduced cis  $\rightarrow$  trans isomerization of cis- $\beta$ -AAN via NMR spectroscopy as well as from a shift in the absorption maximum from 254 nm to 252 nm with an initial increase in absorption intensity. Photolysis in vacuum degassed water gave imidazole as determined by absorption spectroscopy and thin layer chromatography (TLC) analysis. Table III summarizes various spectroscopic and photochemical results for AAN as well as the other molecules studied.

In addition to AAN, we have studied a series of related molecules, both spectroscopically and photochemical. These are  $\beta$ -aminocrotononitrile (ACN), VI; 2-amino-1-propene-1,1,3-tricarbonitrile (APN), VII; 3-dimethylaminoacrylonitrile (DAAN), VIII; and 2-aminocyclopentene-1-carbonitrile (ACPN), IX.



A summary of spectroscopic and photochemical results are given in Table III.

Irradiation of ACN (VI) in water produces 4-methyl imidazole as verified by absorption spectroscopy, TLC and gas chromatography. In the absence of oxygen the quantum yield of formation of the imidazole is  $2 - 3 \times 10^{-5}$  (likely to be a lower limit). Oxygen strongly inhibits the rate of formation of the imidazole and plays an important role in the photodecomposition leading in part at least to  $\text{NH}_4^+$  and  $\text{CN}^-$  (in water solution). Also, there is a dependence on wavelength of excitation for photochemistry in the presence of oxygen.

Irradiation of APN (VII) in water results in a decrease of the principal absorption band (273 nm) and the formation of a weak shoulder in the region of 224 nm. Analysis of the product utilizing TLC followed by absorption spectroscopy strongly indicate a substituted imidazole was formed.

The ACPN (IX) cannot undergo photoisomerization as could all of the other molecules because of the cyclopentene ring. Irradiation of ACPN in water followed by TLC analysis gave a product with an absorption maximum at 208 nm which is in the region typical of imidazole (or methyl substituted ones). Therefore, we believe the product is 4,5 trimethylene imidazole.



In the case of DAAN (VIII) the important question was whether it was necessary to have hydrogen atoms on the amino group in order that photocyclization to an imidazole be possible. Irradiation of a water solution resulted in a new absorption at 208 nm. TLC analysis and comparison with a known sample of 1,2 dimethylimidazole showed that photoproduct was 1,2 dimethylimidazole.

The formation of 1,2 dimethylimidazole from DAAN (VIII) clearly shows that completely alkyl substituted enaminonitriles can undergo photocyclization. Therefore, hydrogen atoms on the amino nitrogen are not a prerequisite for imidazole formation and methyl can migrate (rearrange) in the photolysis reaction.

Except for ACPN (IX) photoisomerization is possible and was observed in all cases except APN (VII) where the isomers are indistinguishable. In addition, this is true for the cases of diaminomaleonitrile (III) and diaminofumaronitrile (IV).<sup>12</sup> Photoisomerization, therefore, competes with photocyclization in the latter two cases as well as for the molecules reported herein.

In order to further verify and quantify this latter point, we measured the relative quantum yield of imidazole formation from ACPN (IX) and found it substantially higher (5-10 times) than from the other enaminonitriles ACN (VI) and DAAN (VIII).

This data plus that of Becker et al<sup>12</sup> confirms that photoisomerization not only competes but is dominant where it can exist.

## IV. SUMMARY OF RESULTING PUBLICATIONS

1. Jaroslav Kolc and Ralph S. Becker, Photochromism of 1,2-Dihydroquinolines, J. Amer. Chem. Soc., 91, 6513 (1969).
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9. Ralph S. Becker, T. Bercovici, and Kong-yi Hong, New Reactions of Paraformaldehyde and Formaldehyde with Inorganic Compounds, J. Molec. Evolution, in press.

Two manuscripts are in the final stage for submission:

1. Henry J. Pownal and Ralph S. Becker, Synthesis, Identification and Photolysis Studies of Cis- $\beta$ -Aminoacrylonitrile.

2. J. H. Hong and Ralph S. Becker, Spectroscopic and Photochemical Study of Enaminonitriles.

TABLE I. SUMMARY OF RESULTS USING HOT HYDROGEN ATOMS

Experiment	Reactants (a) (Pressure in cm Hg)	Lowest Temperature	Irradiation Time	Light Source	Amino Acids Detected	Other Products Detected
I	$\text{CH}_3\text{SH} = 42.5$	30°C	14 days	1 kw Xe lamp	Aspartic	$\text{CH}_3\text{SSH}$ , $\text{CH}_3\text{SSCH}_3$ and two or
	$\text{C}_2\text{H}_6 = 12.5$				Glycine	more amino compounds that are more
	$\text{NH}_3 = 12.5$				Cysteine	acidic than the protein amino
	$\text{H}_2\text{O} = 9$				Valine	acids and some more basic
II	$\text{CH}_3\text{SH} = 42.4$	50°C for	None	None	None	Other amino compounds more
	$\text{C}_2\text{H}_6 = 12.5$	14 days				acidic than all protein amino
	$\text{NH}_3 = 12.5$					acids but no protein amino
	$\text{H}_2\text{O} = 9$					acids <sup>(b)</sup>
III	$\text{H}_2\text{S} = 47.5$	50°C	14 days	1 kw Xe lamp	Aspartic	Sulfur and maybe one amino com-
	$\text{C}_2\text{H}_6 = 12.5$				Glycine	pound more acidic than protein
	$\text{NH}_3 = 12.5$				Glutamic	amino acids possibly some more
	$\text{H}_2\text{O} = 9$				Cysteine	basic
IV	$\text{CH}_3\text{SH} = 37.5$	50°C	14 days	500 w	---	
	$\text{C}_2\text{H}_6 = 37.5$			High pressure		$\text{CH}_3\text{COOH}$ , $\text{C}_2\text{H}_5\text{COOH}$ , $\text{C}_2\text{H}_5\text{OH}^{(c)}$
	$\text{H}_2\text{O} = 9$			Hg lamp		$\text{CH}_3\text{SSCH}_3$ , $\text{CH}_3\text{SSH}$

TABLE I. CONTINUED

Experiment	Reactants (a)	Lowest T Temperature	Irradiation Time	Light Source	Amino Acids Detected	Other Products Detected
V	$\text{H}_2\text{S} = 25$	30°C	21 hours	500 W	Serine	Sulfur and possibly some amino compounds more basic than the protein amino acids
	$\text{NH}_3 = 12.5$				or Threonine	
	$\text{C}_2\text{H}_5\text{OH} = 7$				Glycine	
VI <sup>f</sup>		30°C	37 hours	500 W	Aspartic	Sulfur and possibly one other amino compound which is more acidic than protein amino acids and some more basic ones.
					Valine	
					Glutamic	
					Leucine	
					Isoleucine	
					Proline	
	$\text{H}_2\text{S} = 25$				Serine	
	$\text{NH}_3 = 12.5$				or Threonine	
	$\text{C}_2\text{H}_5\text{OH} = 7$ (2 ml)				Aspartic <sup>f</sup>	
	$\text{H}_2\text{O} = 3.2$				Valine <sup>f</sup>	
					Leucine <sup>f</sup>	
					Isoleucine <sup>f</sup>	
					Glutamic <sup>f</sup>	
					Proline (trace amount) probably <sup>f</sup> alanine <sup>f</sup> Glycine <sup>f</sup>	

TABLE I. CONTINUED

Experiment	Reactants (a)	Lowest Temperature	Irradiation Time	Light Source	Amino Acids Detected	Other Products Detected
VII	$\text{CH}_3\text{SH} = 25$	Room	14 days	1 kw Xe lamp	---	$\text{CH}_3\text{SSH}$ , $\text{CH}_3\text{SSCH}_3$ , and methylamine <sup>d</sup>
	$\text{CH}_4 = 25$	Temperature				
	$\text{NH}_3 = 25$					
	$\text{H}_2\text{S} = 25$					
VIII	$\text{H}_2\text{S} = 25$	50°C	25 hrs.	500 w	Aspartic	Sulfur
	$\text{C}_2\text{H}_5\text{NH}_2 = 25$			High pressure	Glycine	
	$\text{H}_2\text{O} = 9$			Hg lamp	Alanine	
					Leucine	
IX					Isoleucine	
					Serine or Threonine	
	$\text{H}_2\text{S} = 25$	50°C	113 1/2 hrs.	500 w	Aspartic	Sulfur and possibly some amino
	$\text{NH}_3 = 25$			High pressure	Serine	compounds more basic and
	$\text{CH}_4(\text{e}) = 25$			Hg lamp	or Threonine	acidic than the protein
	$\text{H}_2\text{O} = 9$				Glutamic	amino acids
					Proline	

TABLE I. CONTINUED

Experiment	Reactants (a)	Lowest Temperature	Irradiation Time	Light Source	Amino Acids Detected	Other Products Detected
X	$\text{H}_2\text{S} = 37.5$	50°C	14 days	1 kw Xe lamp	---	None
	$\text{H}_2\text{O} = 9.0$					
	$\text{CO} = 37.5$					
	$\text{CO} = 26$	30°C	38 hrs.	500 w	None	$\text{CH}_3\text{CHO}$
	$\text{CH}_4 = 26$			High pressure		$\text{COS}$
XI	$\text{H}_2\text{S} = 26$					$\text{CS}_2$
						$\text{SO}_2$
						$\text{C}_2\text{H}_6$
						Sulfur
						One unidentified
XII <sup>9</sup>	$\text{CO} = 26$	30°C	None	None	None	$\text{COS}^9$
	$\text{CH}_4 = 26$	for 38 hrs.				
	$\text{H}_2\text{S} = 26$					



TABLE I. CONTINUED

Experiment	Reactants (a)	Lowest Temperature	Irradiation Time	Light Source	Amino Acids Detected	Other Products Detected
XIII	$C_2H_4 = 13$	30°C	27 hrs.	500 w	None	$C_2H_5SH$
	$NH_3 = 13$					$C_2H_5NH_2$
	$H_2S = 43$					$C_2H_6$
	$H_2O = 9$ (2 ml)					$(C_2H_5)_2S$

- (a) In all experiments, the first molecule shown ( $\text{H}_2\text{S}$  or  $\text{CH}_3\text{SH}$ ) is the source of the hot H atom by photolysis eq. 5 of text.
- (b) We carefully determined blanks as follows. In one case, after the thermal reaction the same procedure was followed as for all other four peaks were detected prior to aspartic acid and other protein amino acids. In another blank, water plus ammonia used to wash the apparatus after hot H atom reactions was passed alone through the Dowex column. Three peaks were detected prior to aspartic acid and was carefully analyzed and one peak was detected prior to aspartic acid and other protein amino acids. In all cases where any of these peaks apparently appeared from the hot H atom reactions, they were 5-10 times more intense than in the blanks but still were not considered as confirmed reaction products.
- (c) If  $\text{CH}_4$  is used,  $\text{CH}_3\text{OH}$  is produced but analysis for acids were not done.
- (d) If  $\text{C}_2\text{H}_6$  is used, ethylamine is produced.
- (e) Ultra high pure grade, minimum purity is 99.97% (Linde Co.).
- (f) In a similar experiment, 6 protein amino acids were identified and 8 non-protein amino acids verified using gas chromatography-mass spectrometry, see text.
- (g) The amount of COS from the thermal reaction is a factor of 20-25 less than from the hot H atom reaction Experiment XI.

TABLE II. MASS SPECTRAL DATA FOR GLYCINE

m/e	Relative Intensity %	
	STD	Unknown
69	1	1
45	0.98	0.74
43	0.43	0.66
126	0.25	0.43
127	0.20	0.28
41	0.21	0.38
97	0.072	0.074
95	0.062	0.043
154	0.062	0.10

TABLE III.

SPECTROSCOPIC AND PHOTOCHEMICAL PROPERTIES OF VARIOUS ENAMINONITRILES<sup>1</sup>

	ACN	AAN	APN	ACPN	DAAN
% conversion to corresponding imidazole	14	25	50	83	38
Time (min)	145	1850	720	185	513
Photosomerization observed	yes	yes	not distinguishable	no	yes
Molar absorption Coefficient $\times 10^{-4}$ ( $M^{-1}cm^{-1}$ )	1.1 $\pm$ 0.1	1.2 $\pm$ 0.3	1.7 $\pm$ 0.02	1.2 $\pm$ 0.1	2.1 $\pm$ 0.2
Absorption max. (nm)	257	254	273	263	265

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<sup>1</sup>All samples except AAN were irradiated in vacuum degassed water solution with the same light source and with the same geometrical arrangement.

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